

1 **Temporal variations and trend of ground-level ozone based on long-term measurements in**
2 **Windsor, Canada**

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9

10 **Abstract**

11 This study investigates temporal variations and long-term (1996-2015) trends of ground-
12 level O₃ (ozone) and its precursors, NO_x (nitrogen oxides) and volatile organic compounds in
13 Windsor, Ontario, Canada. During the 20-year study period, NO_x, non-methane hydrocarbon
14 concentrations and ozone formation potential decreased significantly by 58%, 61%, and 73%,
15 respectively, while O₃ concentrations increased by 33% (20.3 ppb in 1996 vs. 27 ppb in 2015).
16 Our analysis revealed that the increased annual O₃ concentrations in Windsor were due to 1)
17 decreased O₃ titration (by 50% between 1996 and 2015) owing to declining nitric oxide
18 concentrations, which is suggested by a slightly decreasing trend of annual mean total O₃
19 concentrations after the titration effect is removed, 2) reduced local photochemical production of
20 O₃, because of dwindling precursor emissions, and 3) increased background O₃ level that has
21 more impact on the low-to-median concentrations. The net effect of those factors is decreasing
22 peak O₃ levels during the smog season from May to September, but an overall increasing trend
23 of annual means. These results indicate that the emission control measures are effective in
24 reducing peak ozone concentrations. However, challenges in lowering annual O₃ levels call for
25 long-term collaborative efforts in the region and around the globe.

26

27 **1. Introduction**

28 Ozone (O₃) at the ground-level is a main component of smog. Exposure to high O₃
29 concentrations causes wheezing and shortness of breath, resulting in absence from schools and
30 hospital admissions (USEPA, 2018). People with respiratory diseases, children, and elders are at
31 higher risks from O₃ exposure. Recent studies suggest that long-term exposure to high O₃ levels
32 is associated with permanent lung damage and deaths from respiratory causes (USEPA, 2018).
33 High O₃ concentrations also result in reduced crop yields by inhibiting breathing ability of
34 plants, slowing down the photosynthesis rates, and making plants more susceptible to diseases
35 (IDNR, 2018).

36 As a secondary air pollutant, ground-level O₃ is formed by photochemical reactions between
37 nitrogen oxides (NO_x) and volatile organic compounds (VOCs) in the presence of sunlight.
38 Non-methane hydrocarbons (NMHCs) are more reactive than methane and other VOCs in forming

39 ozone (NAS, 1999); therefore, NMHCs are used to represent O₃ precursors (e.g. Jun et al., 2007;
40 Akimoto et al., 2015). Because the reactivity of each NMHC is different, Carter (1994) and other
41 researchers used O₃ formation potential (OFP) to quantify contributions of individual NMHCs or a
42 group of NMHCs (Jia et al., 2016). Similarly, a study in Hong Kong investigated associations
43 between O₃ and its precursors, i.e. NO_x and 21 NMHCs during 2005-2014 (Wang et al., 2017). O₃
44 concentrations in Hong Kong increased (0.56 ppb/year, p<0.01) while NO_x decreased (-0.71
45 ppb/year, p<0.01). The study further showed that there were no significant changes in NMHCs (-
46 0.03 ppb/year, p>0.1) during the 10-year study period. Nevertheless, the calculated daytime average
47 contribution to O₃ concentrations by aromatics decreased (-0.23 ppb/year, p<0.05), while that by
48 alkenes increased (0.14 ppb/year, p<0.05) and that by alkanes and biogenic VOCs did not change
49 significantly (-0.04 ppb/year, 0.24 ppb/year, respectively, p>0.05) (Wang et al., 2017).

50 In Ontario, Canada, emissions of NO_x and VOCs decreased by 52% (from 651 to 311 kilo
51 tonnes) and 54% (from 789 to 363 kilo tonnes) respectively during 1996-2015 (ECCC, 2018a).
52 However, Ontario-wide O₃ composite mean increased by 22% from 22.4 ppb in 1996 (MOE, 2006)
53 to 27.4 ppb in 2015 (MOECC, 2017). Previous studies showed that changes in O₃ concentrations
54 were attributed to background O₃ and changes in photochemical O₃ production caused by the
55 decrease in NO_x and VOC concentrations (e.g. Shin et al., 2012). Because NO (nitric oxide) reacts
56 with O₃ to form NO₂ (nitrogen dioxide) and O₂, also known as NO titration, decreased NO
57 concentrations may lead to increases in O₃ concentrations due to weakened titration effect (Sicard et
58 al, 2011; Akimoto et al., 2015). To remove the impact of the NO titration on ambient O₃
59 concentrations, “total ozone” (TO) was previously employed in trend analysis. For example,
60 Akimoto et al. (2015) used TO in their ambient ozone study in four areas in Japan where O₃
61 concentrations were high (i.e., Tokyo, Nagoya, Osaka, and Fukuoka). During the 20-year study
62 period, NO concentrations decreased from 16 ppb in 1990 to 6 ppb in 2010. The increasing rates of
63 annual TO (0-0.22 ppb/year) were much smaller than those of O₃ (0.22-0.37 ppb/year) in the four
64 areas during 1990-2010. The authors concluded that the decrease in the NO titration effect was one
65 of the causes for the increased O₃ concentrations in Japan.

66 Recently, continuous O₃ observations (2-years or longer) from more than 9,600 stationary
67 platforms around the world were assembled to assess a suite of metrics relevant to its impact on
68 human health, vegetation, and climate under the International Global Atmospheric Chemistry
69 (IGAC)’s Tropospheric Ozone Assessment Report (TOAR) project (Schultz et al., 2017; IGAC,

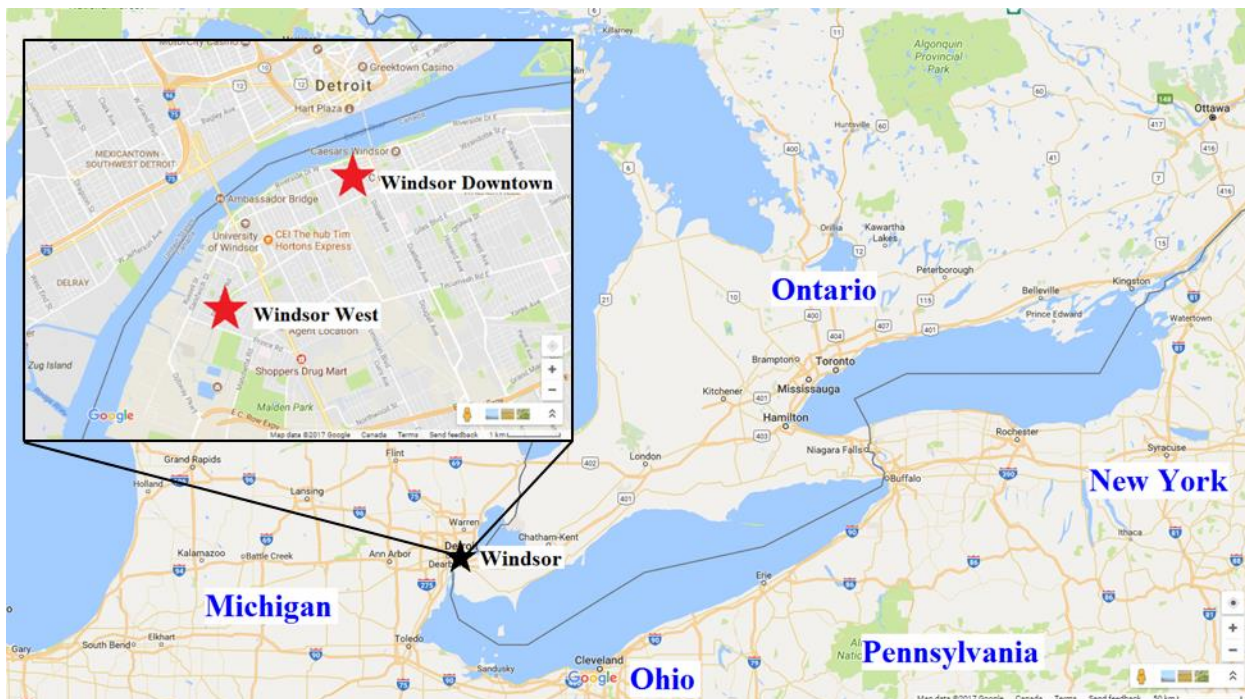
70 2018). Using 2010–2014 means from over 3300 vegetation sites, the highest ozone levels were
71 found in mid-latitudes of the northern hemisphere, including southern USA, the Mediterranean
72 basin, northern India, north, north-west and east China, the Republic of Korea, and Japan (Mills et
73 al., 2018). In a study of over 2,000 monitoring sites worldwide, negative (i.e. decreasing) trends in
74 peak O₃ concentrations (i.e. 4th highest daily maximum 8-hour average) were observed at most
75 North American sites and at some European sites, with very few sites exhibited positive trends
76 (Fleming et al., 2018). Similar studies reported that O₃ levels (monthly mean of the daytime average
77 and monthly mean of the daily maximum 8-hour average) continued to decrease significantly over
78 eastern North America and Europe, while Asia experienced increasing O₃ concentrations through the
79 end of 2014 (Chang et al., 2017; Gaudel et al., 2018). In Eastern North America, summertime
80 daytime averages and daily maximum 8-hour concentrations declined at a slower rate at urban sites
81 than at rural sites during 2000-2014 (Chang et al., 2017). Those studies showed that, over North
82 America and Europe, decreasing peak O₃ levels is attributable to reduction in precursor emissions
83 and a relatively slower decreasing rate at urban locations suggests weakened O₃ titration. In Asia,
84 growing precursor emissions led to increasing ozone concentrations.

85 Built on our understanding of spatial variations (Fleming et al., 2018; Mills et al., 2018), this
86 study evaluated temporal variations and trends of ground-level O₃ and its precursors (NO_x and
87 VOC) in Windsor, an urban location in Southern Ontario, Canada, during the 20-year study period
88 of 1996-2015. The main objective was to identify the driving force of long-term trends of O₃
89 concentrations in Windsor during the past 20 years, as well as seasonal and diurnal variations.
90 Findings of this study will shed light on the effectiveness of emission control policies and help
91 develop feasible approaches to reducing O₃ concentrations in this region.

92 **2. Methodology**

93 **2.1 Selection of station in Windsor**

94 There are two air quality monitoring stations in Windsor: Windsor Downtown and Windsor
95 West which are 3.5 km apart (Figure 1). Both stations monitor O₃ and a number of common air
96 pollutions (e.g. NO, NO₂, NO_x, SO₂, and PM_{2.5}) (MECP, 2018). The Windsor Downtown
97 station was selected in this study due to 1) fewer invalid or missing O₃ values (1824 vs. 2660
98 during 1996-2015), and 2) a longer record of NO, NO₂, and NO_x data available (1996-2015)
99 compared to the Windsor West station (2001-2015). Twenty-four-hour VOC samples were
100 collected once every six days at the Windsor West station (ECCC, 2016).



101

102 **Figure 1.** Air quality monitoring stations in Windsor, Ontario, Canada

103

104 **2.2 Data sources**

105 Hourly O₃, NO, NO₂, and NO_x concentrations in Windsor (1996-2015) were obtained from
 106 the Ontario Ministry of the Environment, Conservation and Parks (MECP). Twenty-four-hour
 107 VOC data at Windsor West station during 1996-2015 were downloaded from National Air
 108 Pollution Surveillance (NAPS) website (ECCC, 2018b).

109 **2.3 Data processing**

110 **2.3.1 O₃, NO, NO₂, NO_x, and VOC concentrations and ratios**

111 Numbers of data flags “-999” (i.e., invalid data), blank cells, and “0” data points in hourly O₃,
 112 NO, NO₂, and NO_x concentrations were counted by year. Then data flags “-999” were replaced
 113 with blank cells to maintain consecutive date/time for individual pollutants. If the total
 114 percentage of data flags and blank cells is greater than 40% (3504 hour/year) in a year, data in
 115 that year is considered invalid and excluded from further analysis. This is the case for hourly
 116 NO, NO₂, and NO_x concentrations in 2003. Results of data screening can be found in Zhang
 117 (2016) and in the Supplemental Materials (Table S1).

118 There are 176 VOC compounds reported in the NAPS dataset, of which 118 were used in this
119 study. Missing samples were identified by comparing the sampling schedule with the dates of
120 available samples in each year. Blank and “0” cells were counted for individual compounds in
121 each year. A compound is excluded from analysis if the total number of blank and “0” cells is
122 greater than 70% during the study period of 1996-2015. Blank and “0” cells were also counted
123 for each sample. Samples with less than 60% compounds registered valid readings were
124 removed. To reduce the undue influence of a few unusual events with extremely high
125 concentrations, outliers were identified and removed.

126 Sixteen NMHCs were excluded from analysis, because less than 30% of samples had valid
127 readings. Thus, 102 compounds were retained for further analysis. Out of 877 samples, 14 were
128 excluded. The rest 863 samples each had at least 60% compounds with valid readings (ranged
129 64%-100%, mean=88%, median=91%) and they were used to calculate total NMHCs and OFPs.
130 Daily NO_x/total NMHCs ratios (referred as NO_x/VOC ratios hereafter) were calculated for the
131 dates when VOC data are available. Hourly NO₂/NO_x ratios were calculated as well.

132 **2.3.2 Total O₃ concentrations**

133 Following Akimoto et al. (2015), TO in Windsor were calculated with equation (1),
134

$$\begin{aligned} 135 \quad [TO] &= [O_3] + [NO_2] - 0.1 * [NO_x] \\ 136 \quad &= [O_3] + [DO_3] \end{aligned} \quad (1)$$

137 where DO₃ ([NO₂] - 0.1 * [NO_x]) represents loss of O₃ due to in situ NO titration; [O₃], [NO₂], and
138 [NO_x] are hourly concentrations; and the constant 0.1 is the fraction of NO₂ in primary NO_x
139 emissions (Itano et al., 2007). In this study, the NO₂ fraction was determined from the slopes of
140 regression of [O_x] (= [O₃] + [NO₂]) vs. [NO_x] in Windsor in each year during the morning NO
141 and NO₂ peak hours (from 5:00 to 8:00) as described in Kurtenbach et al. (2012). The 20-year
142 average fraction was 0.1, consistent with that in the previous O₃ study in Japan (Itano et al.,
143 2007).

144 **2.3.3 NMHC concentrations and ozone formation potential**

145 OFPs for individual VOC compounds were calculated using equation (2) as described in Yan
146 et al. (2017),

147
$$\text{OFP}_i = \text{Conc}_i * \text{MIR}_i \quad (2)$$

148 where Conc_i ($\mu\text{g}/\text{m}^3$) is the ambient concentration of the i th NMHC, and MIR_i is the
149 corresponding maximum incremental reactivity coefficient in the unit of grams ozone formed
150 per gram VOC added in the system (Carter, 1999). OFPs for individual samples in each year
151 were calculated.

152 **2.4 Temporal variation and trend**

153 The analysis of variance (ANOVA) was used to determine whether there were statistical
154 differences in O_3 and TO concentrations between weekdays and weekends. Linear regression
155 was employed to examine long-term (1996-2015) trends of 1) annual means and means in the
156 smog (May-September) and non-smog season (October-April) for O_3 and TO, 2) annual mean
157 for NO, NO_2 , NO_x , OFP, DO_3 , NMHC concentrations and the ratio of NO/NO_x , 3) various
158 annual percentile levels (5th, 25th, 50th, 75th, and 95th) of hourly O_3 and TO.

159 Hourly O_3 , TO, and DO_3 concentrations do not follow a normal distribution. Thus, the Mann-
160 Kendall test, a non-parametric trend detection method (Gilbert, 1987) was used to detect long-
161 term trends in each month of a year and at each hour in a day. Sen's method (Sen, 1968) was
162 used to estimate the slope of seasonal and diurnal trends when the trend is significant at the 95%
163 level. Long-term trends of O_3 and TO in Windsor were compared to quantify the impact of the
164 NO titration on O_3 concentrations.

165 All analysis outlined in sections 2.3-2.4 were carried out in Minitab release 16 (Minitab Inc.,
166 State College, Pennsylvania, USA) and MATLAB release 2017a (The MathWorks, Inc., Natick,
167 Massachusetts, USA).

168 **3. Results and discussion**

169 **3.1 General statistics**

170 As shown in Table 1, the 20-year mean O_3 concentration was 24 ppb in Windsor. Higher O_3
171 levels were observed in the smog season than the non-smog season, reflecting photochemical
172 production under sunny and warm conditions. TO concentrations were higher than O_3
173 concentrations in all seasons and at all concentration percentile levels because TO includes the
174 fraction of O_3 lost through the NO titration. TO concentrations showed lower variability (i.e.,

175 lower coefficient of variation) than O₃ concentrations, which is expected because O₃ reacts with
 176 NO while TO is not affected by the NO titration (Akimoto et al., 2015).

177

178 **Table 1.** General statistics of O₃ and TO concentrations in Windsor during 1996-2015. (SD and
 179 CV stand for standard deviation and coefficient of variation, respectively)

Pollutant	Season	Mean (ppb)	SD (ppb)	CV (%)	Min (ppb)	25 th (ppb)	Median (ppb)	75 th (ppb)	Max (ppb)	Sample size
O ₃	All months	24	17	71	0	11	22	34	128	171624
	Smog	32	19	59	0	18	30	44	128	72387
	Non- Smog	18	13	71	0	7	17	27	85	99237
TO	All months	39	14	36	0	30	37	46	138	161459
	Smog	45	17	37	0	33	43	54	138	68270
	Non- Smog	35	11	29	0	28	34	41	118	93189

180

181 3.2 Diurnal, seasonal and weekday-weekend variation

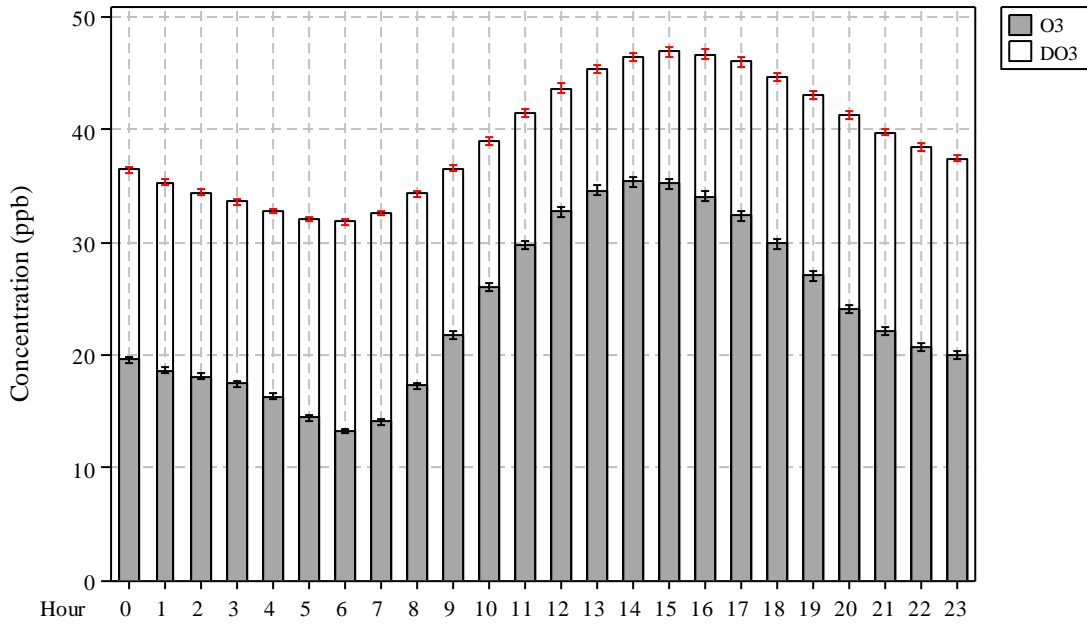
182 3.2.1 Diurnal variation

183 Diurnal variation of O₃ concentrations in Windsor during 1996-2015 is shown in Figure 2a
 184 and Table S2. There was a gradual increase in O₃ concentrations from the hour 6:00 to 14:00
 185 local time, and a gradual decrease from the hour 15:00 to 6:00 next day. A similar trend was
 186 observed for TO. The diurnal variations for O₃ and TO indicate O₃ photochemical production
 187 was enhanced by increased solar radiation and temperature (So and Wang, 2003). DO₃ followed
 188 an opposite trend than O₃, i.e. lower at noon to afternoon (11.2 ppb from the hour 11:00-15:00)
 189 than that at other hours of the day (16.2 ppb), suggesting that relative loss due to the titration
 190 effect was reduced when O₃ concentrations were high.

191 O₃ concentrations were higher during the smog season than in the non-smog season
 192 especially around noon due to photochemical production (Fig 2b and Fig 2c). DO₃ levels were
 193 lower throughout the day in the smog season, suggesting relative loss due to the titration effect
 194 was reduced when O₃ concentrations were high. Furthermore, TO (O₃+DO₃) diurnal variation
 195 was rather smooth in the non-smog season due to weak photochemical production of O₃.

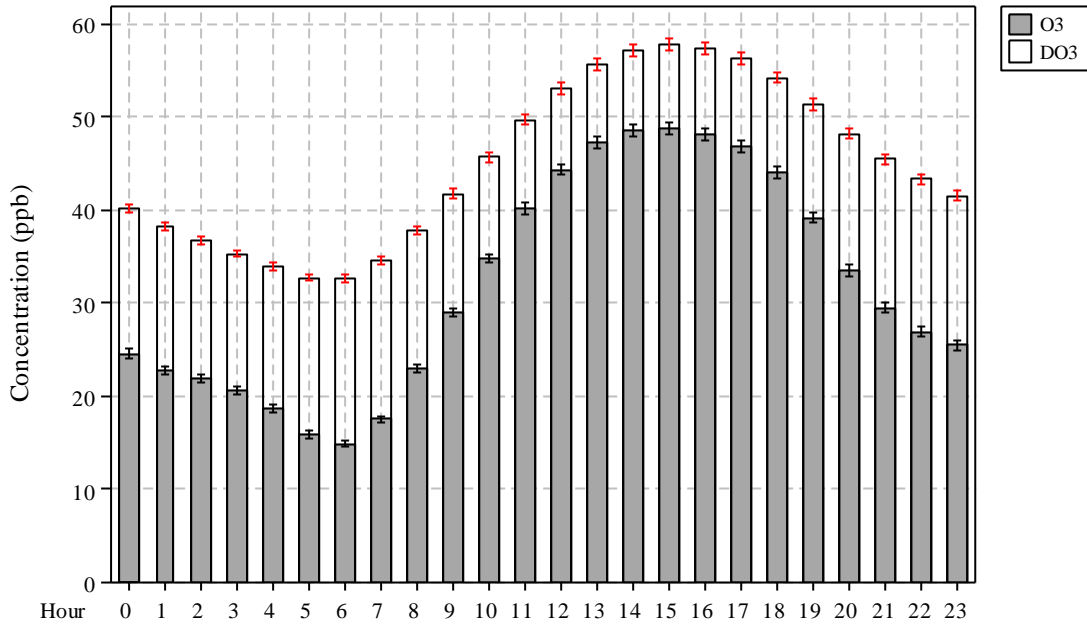
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(a) Diurnal variability of O₃ and DO₃ at Windsor during 1996-2015
95% CI for the Mean

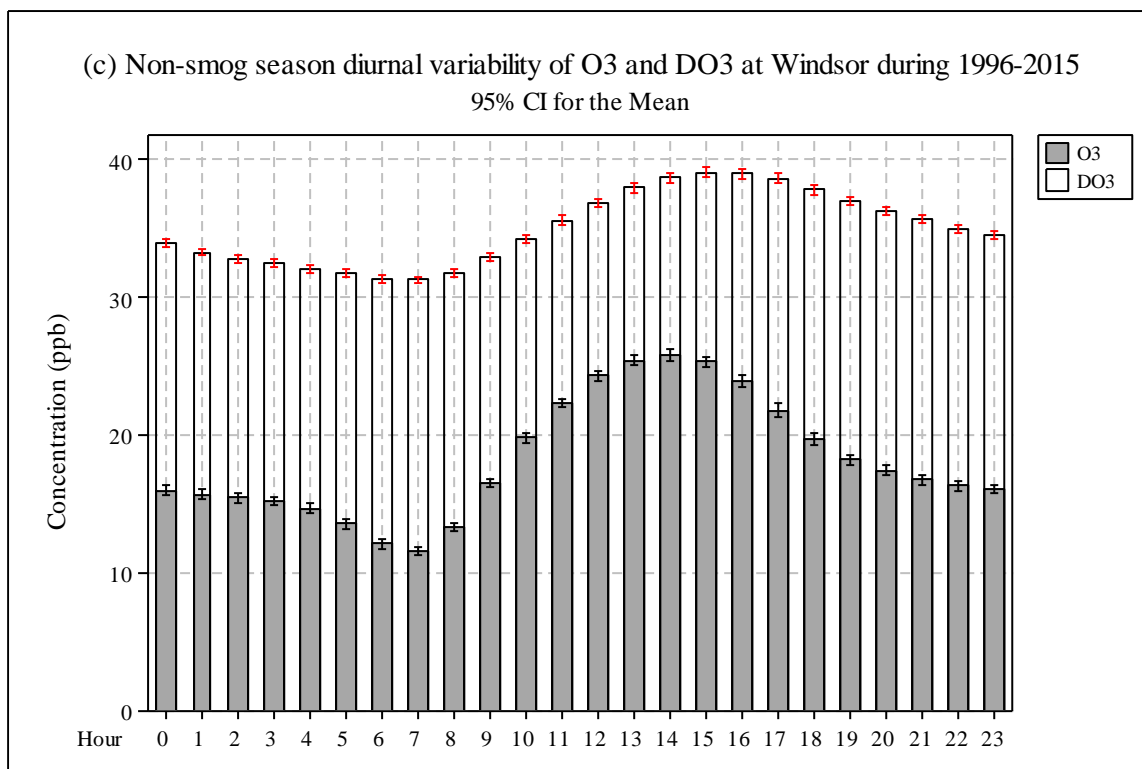


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(b) Smog season diurnal variability of O₃ and DO₃ at Windsor during 1996-2015
95% CI for the Mean



198



199

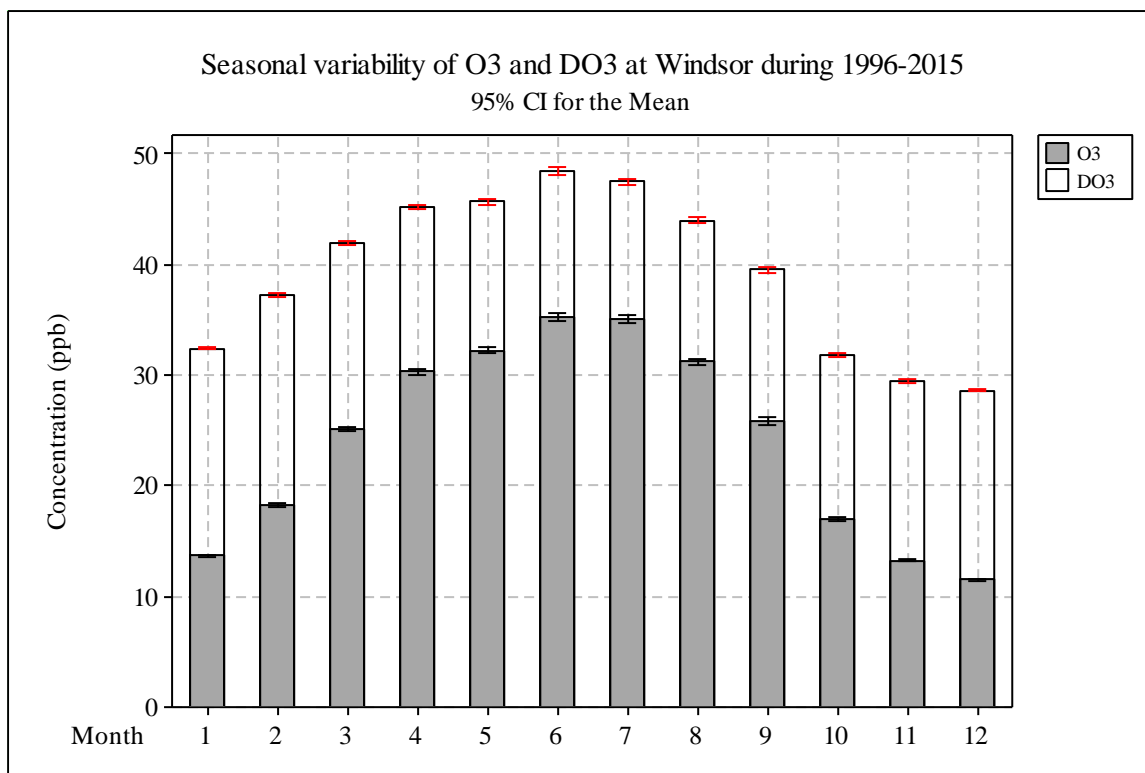
200 **Figure 2.** Diurnal O₃ and DO₃ concentrations during 1996-2015 in Windsor for (a) all months,
201 (b) smog season, and (c) non-smog season.

202

203 3.2.2 Seasonal variation

204 Monthly O₃ concentrations increased from January to May, reaching peak values in June
205 and July, then decreased from July till the minima in December (Fig 3 and Table S3). This
206 seasonal pattern is similar to that of solar radiation and ambient temperature, which control the
207 photochemical production rate of O₃. A similar seasonal variation was observed for TO, but DO₃
208 followed an opposite trend than O₃, i.e. higher in non-smog season (16.6 ppb) and lower during
209 smog season (13.1 ppb). Similar to the diurnal variation, relative loss due to the titration effect
210 appears reduced when weather conditions favored O₃ formation. The seasonal O₃ pattern
211 observed in Windsor is consistent with the study by Gaudel et al. (2018) reporting that in North
212 America the maximum O₃ daytime averages occurred in spring/summer and the minimum
213 values were found in autumn/winter during 2010-2014.

214



215

216 **Figure 3.** Monthly mean O₃ and DO₃ concentrations during 1996-2015 in Windsor.

217

218 3.2.3 Weekday-weekend variation

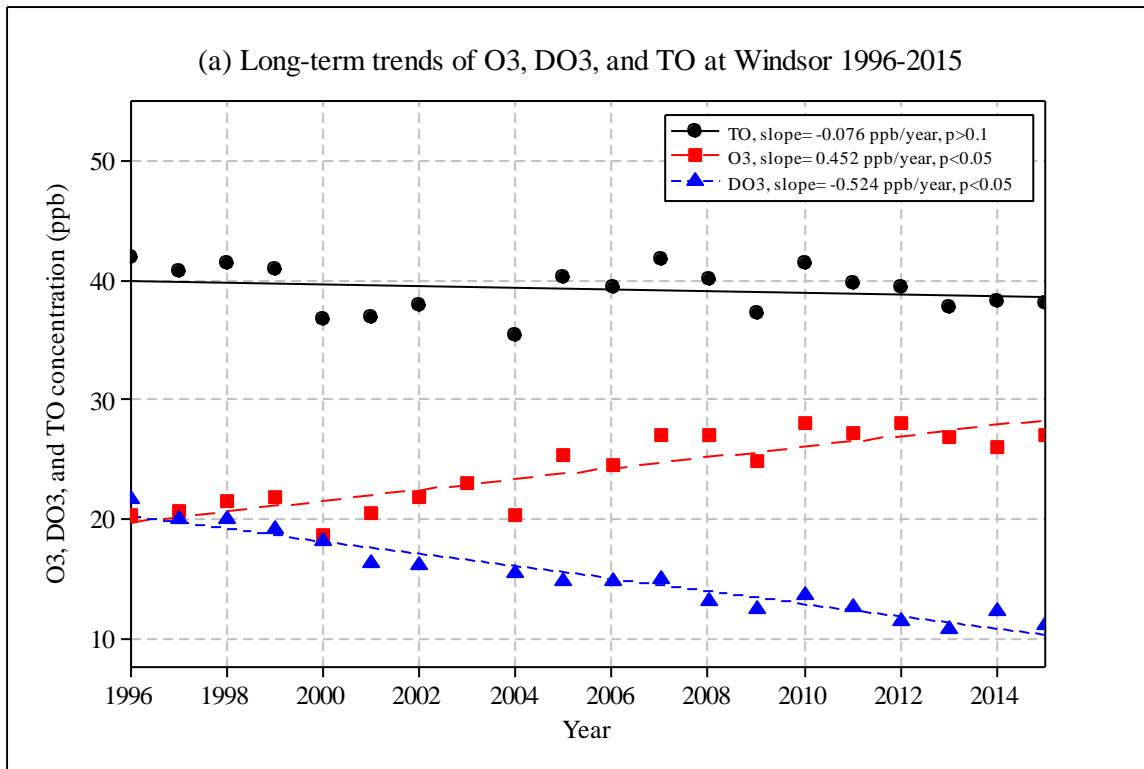
219 ANOVA indicates that O₃ concentrations on weekends (25.9 ppb) were statistically higher
 220 (p<0.05) than on weekdays (23.3 ppb). NO concentrations were lower on weekends (6.5 ppb)
 221 than on weekdays (9.6 ppb) due to less vehicular and industrial activities. Therefore, high O₃
 222 concentrations on weekends were likely attributed to decreased NO emissions and weakened
 223 titration effect as reported by other researchers (Koo et al., 2012). This is supported by much
 224 comparable TO concentrations between weekdays and weekends (39.2 ppb vs. 39.5 ppb, p<0.05)
 225 which remove the titration effect. Differences in O₃ levels between weekday and weekend were
 226 also reported in other studies, e.g. in Nepal (Pudasainee et al., 2006) and Ontario, Canada
 227 (Huryn and Gough, 2014).

228 **3.3 Long-term trend**

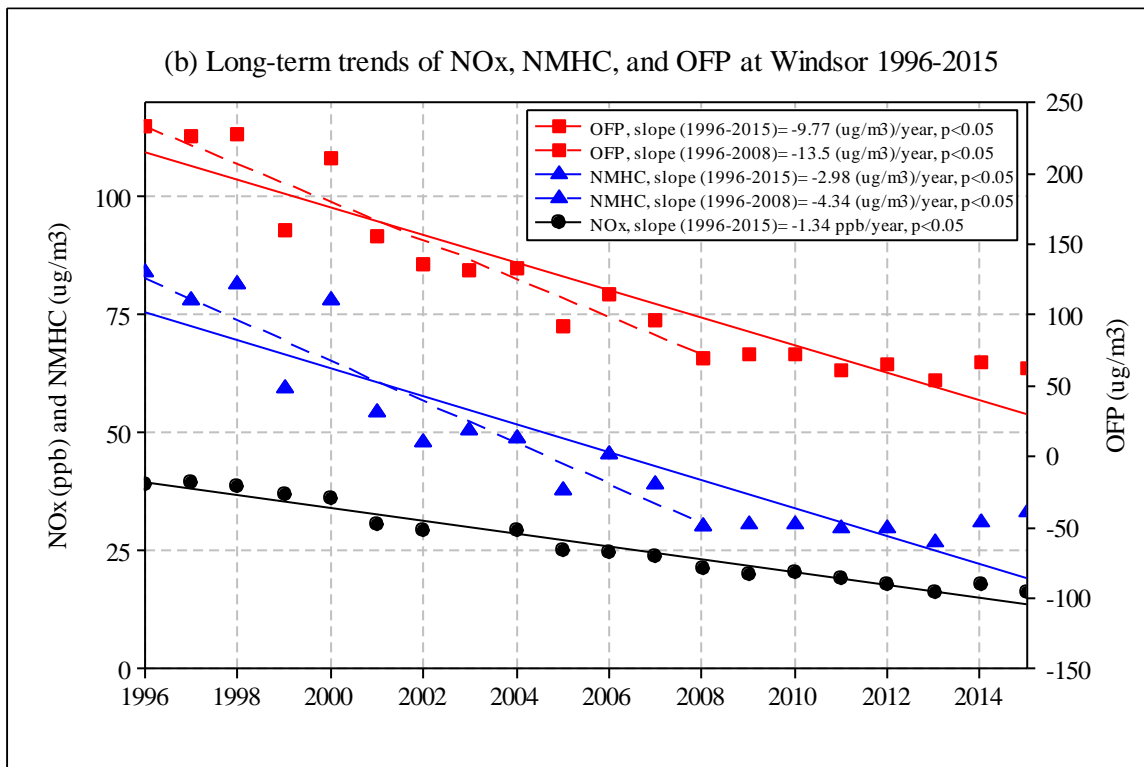
229 **3.3.1 Trends of annual NO_x, NMHC, ozone formation potential, O₃ and TO**

230 During 1996-2015, annual mean O₃ concentrations increased significantly (0.452 ppb/year,
231 Figure 4a) while annual mean DO₃ concentrations decreased at a greater rate (-0.524 ppb/year).
232 Consequently, TO concentrations decreased slightly (-0.076 ppb/year, but not significant). In
233 other words, O₃ decreased slightly when the NO titration effect is removed, suggesting that the
234 decreased NO titration effect is one of the reasons for the increased O₃ concentrations in
235 Windsor.

236



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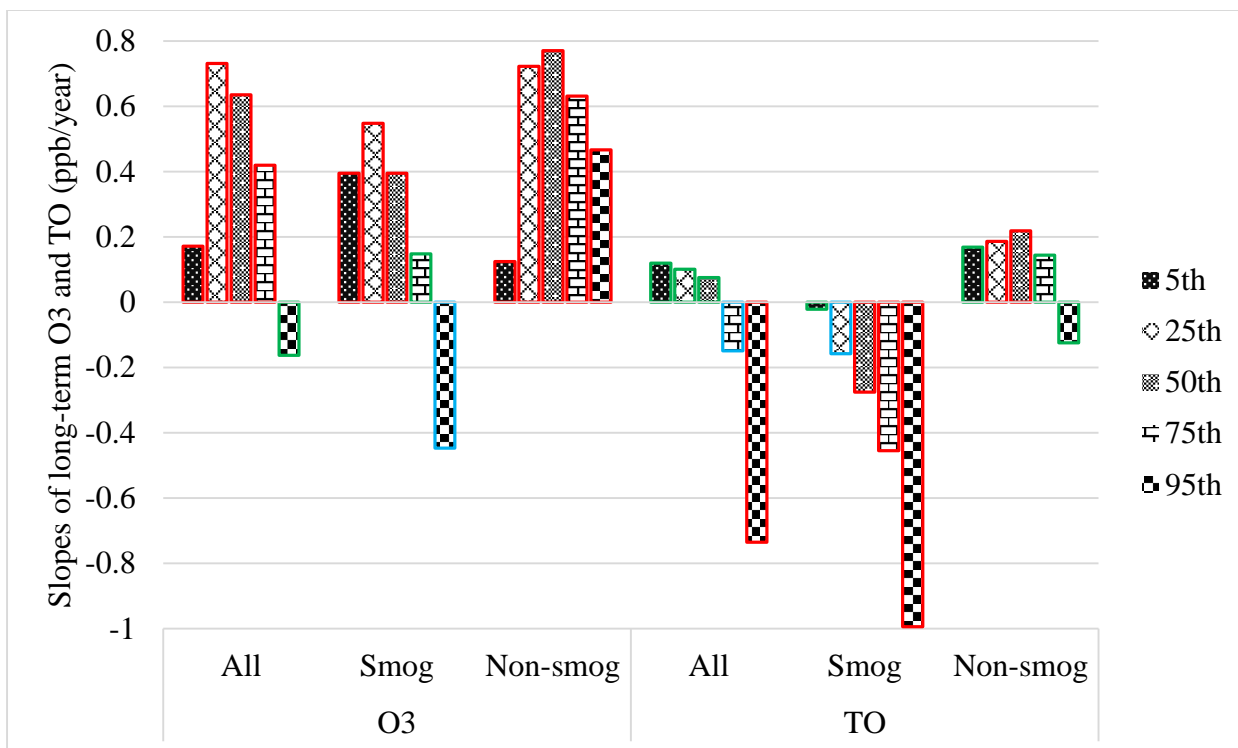
238 **Figure 4.** Annual mean concentrations for (a) O₃, DO₃, and TO, and (b) NO_x, NMHC, and
239 ozone formation potential (OFP) in Windsor during 1996-2015.

240 Significantly decreasing trends were observed in Windsor for annual mean NO_x (-1.34
241 ppb/year), NMHC (-2.98 µg/m³/year), and OFP (-9.77 µg/m³/year) during the 20-year study
242 period (Figure 4b). The percent decreases were 58%, 61%, 73% for NO_x, NMHC, and OFP,
243 respectively, indicating effective emission control. It should be noted that during 1996-2008,
244 some pollutants were changing at greater rates compared with the 20-years trend, including O₃
245 (0.55 ppb/year), NMHC (-4.34 µg/m³/year) and OFP (-13.5 µg/m³/year). After 2008,
246 concentrations of O₃, NMHC, and OFP leveled off, while NO_x and DO₃ concentrations
247 continued to decrease.

248 The decreased NO titration effect was further investigated by examining the ratio of NO/NO_x
249 (Figure S1). Significantly decreased NO (-0.73 ppb/year) and NO₂ (-0.66 ppb/year) were
250 observed during the study period. Furthermore, the NO/NO_x ratio decreased from 0.34 in 1996
251 to 0.16 in 2015 with an average rate of -0.012/year, supporting the decrease in the NO titration
252 effect in Windsor. Our results are consistent with studies in other countries. For example,
253 NO₂/NO_x ratio increased from 0.08 in 2005 to 0.15 in 2010 in Japan (Itano et al., 2014),
254 implying a decreased NO/NO_x ratio. The NMHC/NO_x ratios did not change much during the
255 20-year study period (min=0.96, max=1.3, mean and median=1.1). The low VOC to NO_x ratios
256 (<5) suggest that the study area is VOC limited, thus reduced NO_x emissions may lead to
257 increased O₃ concentrations (Sillman, 1999; USEPA, 2000).

258 **3.3.2 Ozone and TO trends at various percentile levels**

259 Figure S2 depicts long-term O₃ and TO trends at 5th, 25th, 50th, 75th, and 95th percentiles in
260 Windsor during 1996-2015. The slopes of linear regression in three scenarios (i.e., all months,
261 the smog season, and the non-smog season) are summarized in Figure 5 and Table S4. Peak O₃
262 concentrations (i.e., 95th percentile) decreased during the smog season and all-month, suggesting
263 reduced precursor emissions and photochemical production. O₃ at all other percentile levels in
264 all three cases had increased, with higher rates at 25th and 50th percentiles. The 25th percentile of
265 O₃ concentrations were commonly considered as a background value (Lin et al., 2000; Aleksic et
266 al., 2011; Parrington et al., 2013). Peak TO concentrations (95th percentile) decreased, especially
267 during the smog season, due to effective emission control of O₃ precursors. TO concentrations
268 increased at all other percentile levels during the non-smog season when O₃ photochemical
269 production was limited, suggesting rising background O₃ concentrations.



270

271 **Figure 5.** Slopes of long-term O₃ and TO trends at various percentile levels in all months, smog
 272 season, and non-smog season in Windsor during 1996-2015. (red border: significant at p<0.05,
 273 blue border: significant at p<0.1, green border: not significant, i.e. p>0.1)

274

275 In the smog season, O₃ concentrations increased at the 5th-75th percentile levels while TO
 276 concentrations decreased with a greater rate at higher percentile levels, supporting that the
 277 decrease in NO titration is one of the causes of increasing O₃ in Windsor. In terms of peak O₃
 278 concentrations (95th percentile), the decreasing rate of TO (-1.0 ppb/year) is more than twice that
 279 of O₃ (-0.45 ppb/year). In other words, when the effect of NO titration is removed, peak O₃
 280 concentrations decreased more intensely due to reduced emissions of O₃ precursors. During the
 281 non-smog season, the increasing rates of TO at 5-75th percentiles were much slower than those
 282 of O₃. The results suggest that the decreased NO titration effect could be one of the causes for
 283 slower decrease of peak O₃ in the smog season and increase of O₃ at low-to-high percentiles
 284 during both the smog and non-smog seasons.

285 The decreasing trend of the 95th percentile O₃ levels in Windsor is consistent with the
 286 decreasing concentrations at upper end of the distribution across the United States (Simon et al.,

287 2014), which evaluated maximum daily 8-hour average O₃ at over 1,000 sites during 1998–2013
288 when NO_x and VOC emissions were decreasing. The declining peak O₃ is also evident in the
289 study of the 4th highest daily maximum 8-hour concentrations during 2000-2014 by Fleming et
290 al. (2018), which indicated that up to 70% of North America stations experienced significant
291 negative trends ($p < 0.05$). The results of the seasonal O₃ trends in Windsor are consistent with
292 previous studies. For instance, Simon et al. (2014) reported that the declining trends were more
293 pronounced in summer than winter, and that increasing O₃ trends at all percentiles were found in
294 both smog and non-smog seasons except for decreasing peak values at urban sites of the East
295 North Central region (close to Windsor) (Simon et al., 2014). Moreover, Gaudel et al. (2018)
296 reported the increasing O₃ levels across North America in winter time (December, January, and
297 February).

298 3.3.3 Monthly and diurnal rates of change for ozone and TO

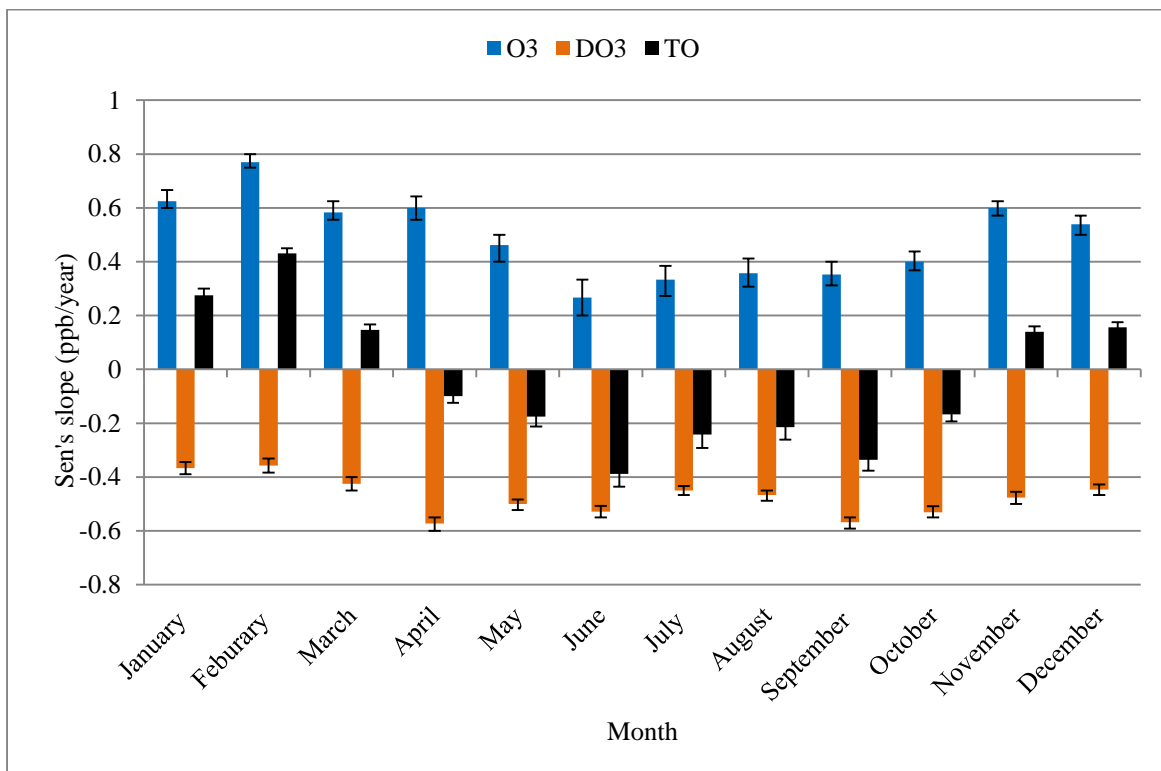
299 This section further investigates which hour(s) of a day and which month(s) of a year
300 experienced greater or less changes in O₃ concentrations during the 20-year study period, and to
301 what degree those changes could be explained by the change in the NO titration effect. The
302 estimated month-of-year slopes by Mann-Kendall and Sen's test during 1996-2015 are shown in
303 Figure 6. The rates of change during the smog and non-smog seasons are summarized in Figure
304 S3.

305 The increased O₃ levels in non-smog season (mean=0.58 ppb/year, Fig S3) suggest reduced
306 titration effect and rising background O₃ levels since local photochemical production of O₃ is
307 limited. Analysis of ambient data conducted by USEPA demonstrated that mid-tropospheric O₃
308 concentrations in the U.S. and globally have increased over the past two decades by 0.4 ppb/year
309 (USEPA, 2015). Along the Pacific Coast, the rate of increasing background O₃ was estimated to
310 be 0.5–0.8 ppb/year during 1985-2002. This trend of ground-level O₃ is consistent with the rate
311 of increase (0.51 ppb/year, 1994 to 2002) derived using aircraft measurements (Jaffe et al.,
312 2003). Another reason of increased O₃ is the decreased titration effect. A study in the South-
313 Eastern France demonstrated that the decrease in the NO titration effect could be one of the
314 reasons for increased O₃ concentrations in cold months (Sicard et al, 2011). The slower
315 increasing rate of O₃ in smog season (0.32 ppb/year, Fig S3) is a result of increased background
316 O₃ levels, decreased titration effect as well as reduced local photochemical O₃ production and

317 regional transport (MOECC, 2017). A similar trend of a greater rate of increasing composite
318 mean at 19 sites across Ontario in summer (49%) than in winter (14%) during 1991-2010 was
319 largely attributable to the reductions in local NO_x emissions and the rising global background
320 ozone levels (MOE, 2012).

321 O₃ concentrations increased while DO₃ concentrations decreased in all months during 1996-
322 2015 (Fig 6). During non-smog season, the increasing rate of O₃ (0.58 ppb/year, Fig S3) was
323 higher than the decreasing rate of DO₃ (-0.46 ppb/year). In other words, there was an additional
324 increase in O₃ beyond the decreased titration effect. After the NO titration effect is removed, TO
325 concentrations increased in non-smog season (0.13 ppb/year, Fig 6), suggesting rising
326 background O₃ levels. In smog season, the increasing rate of O₃ (0.32 ppb/year) was lower than
327 the decreasing rate of DO₃ (-0.50 ppb/year). TO concentrations had decreased in the smog
328 season (-0.27 ppb/year, Fig 6), attributable to the decreased regional O₃ production.

329



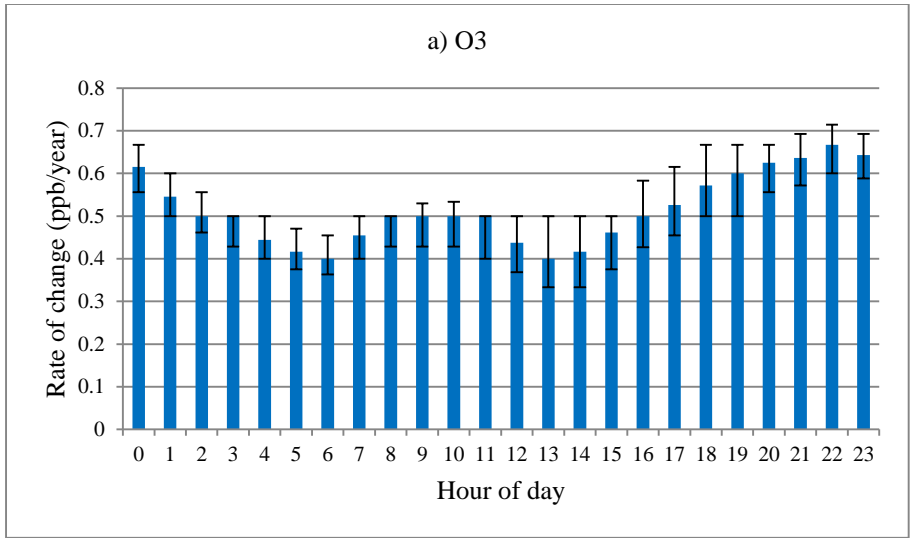
330

331 **Figure 6.** Monthly rates of change during 1996-2015 for O₃, DO₃, and TO.

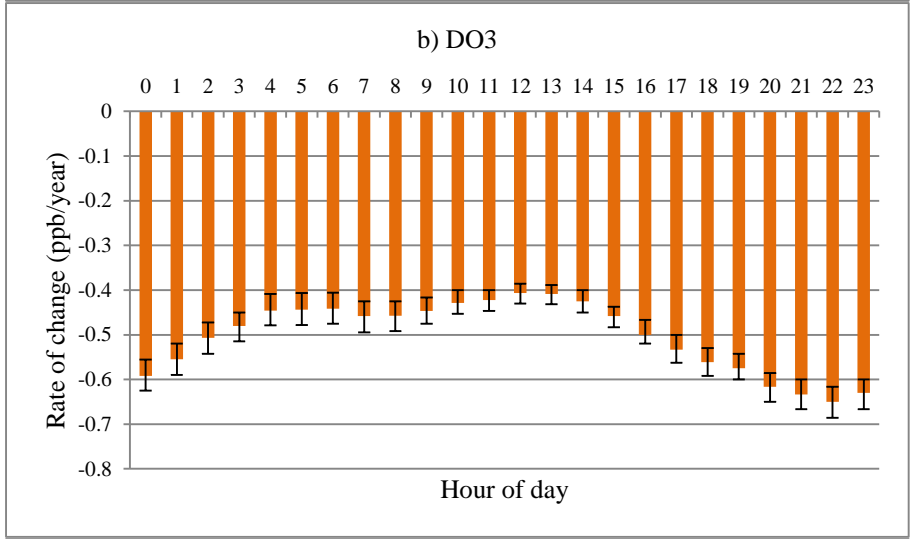
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333 On an hourly basis, greater increasing rates in O₃ concentrations were observed at evening
334 and night hours (18:00-3:00) in comparison with early morning and daytime (4:00-17:00) as
335 shown in Figure 7. The two minima in the morning at 6:00 and 13:00 coincided with the lowest
336 and highest O₃ concentrations in a day, which were caused by different rates of change in smog
337 and non-smog seasons (see below). Overall, O₃ increased while DO₃ decreased at all hours in a
338 day during 1996-2015. The diurnal pattern of increasing rates for O₃ almost mirrored that of
339 decreasing rates for DO₃. In other words, the increase in O₃ concentrations could be explained
340 largely by the decreased NO titration effect. At most hours, the increasing rates of O₃ were
341 higher than the decreasing rates of DO₃ especially in morning hours (6:00-12:00). Overall, TO
342 concentrations increased slightly during daytime while decreased a little in evening.

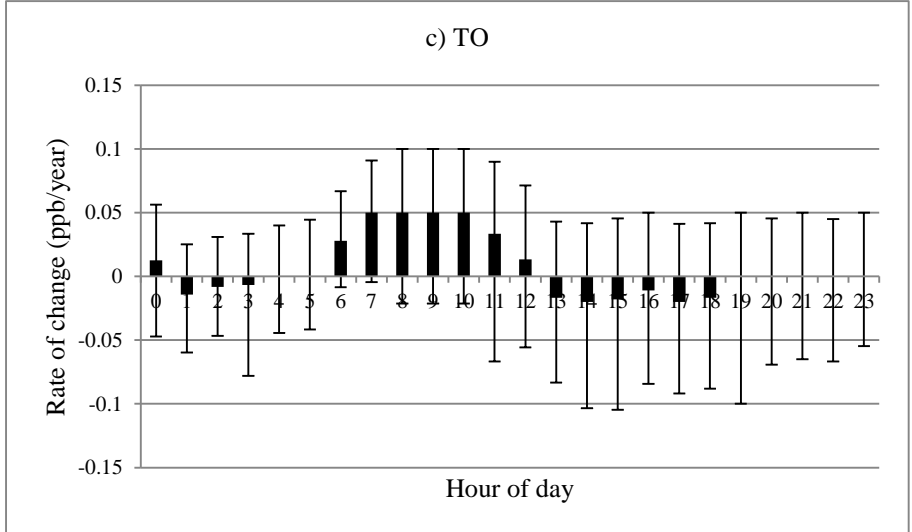
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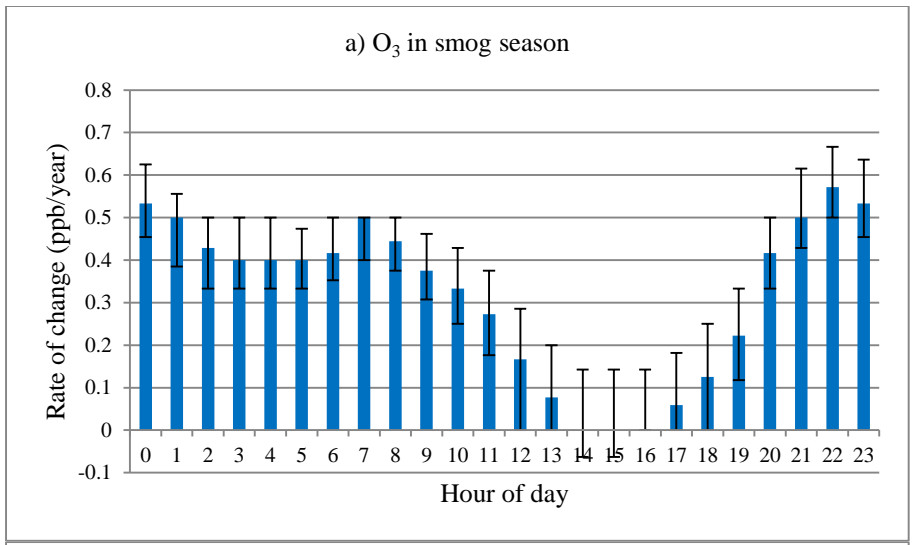
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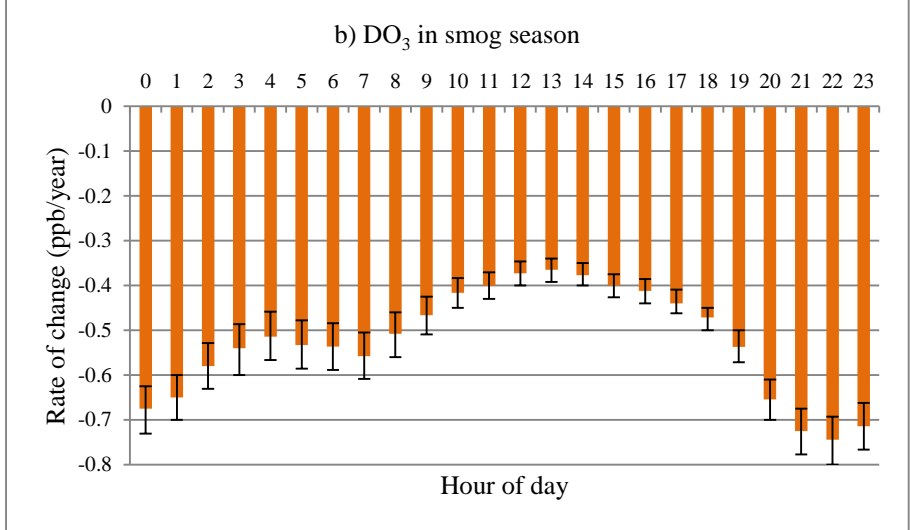
Figure 7. Rate of change by hour-of-day for all months during 1996-2015 for a) O₃, b) DO₃, and c) TO.

349 O₃ and DO₃ concentrations showed different diurnal patterns during the smog season
350 (Figure 8). O₃ concentrations increased while DO₃ concentrations decreased at all hours as in the
351 case of all months. During daytime (9:00-19:00), there was a sharp decline in the rates of change
352 for O₃ till peak O₃ hours (14:00-16:00) followed by a speedy recovery. The peak hour O₃
353 concentrations have not changed much during the last 20 years, and daytime ozone levels have
354 increased with a much slower rate (9:00-19:00, mean=0.15 ppb/year) compared with nighttime
355 (20:00-8:00, mean=0.46 ppb/year). The daytime DO₃ decreasing trend is similar, however, with
356 a less variability. The increasing rate of O₃ is lower than the decreasing rate of DO₃, and TO
357 concentrations decreased at all hours, especially during the afternoon and early evening (14:00-
358 19:00). It suggested decreased photochemical O₃ formation during the smog season due to
359 emission reduction.

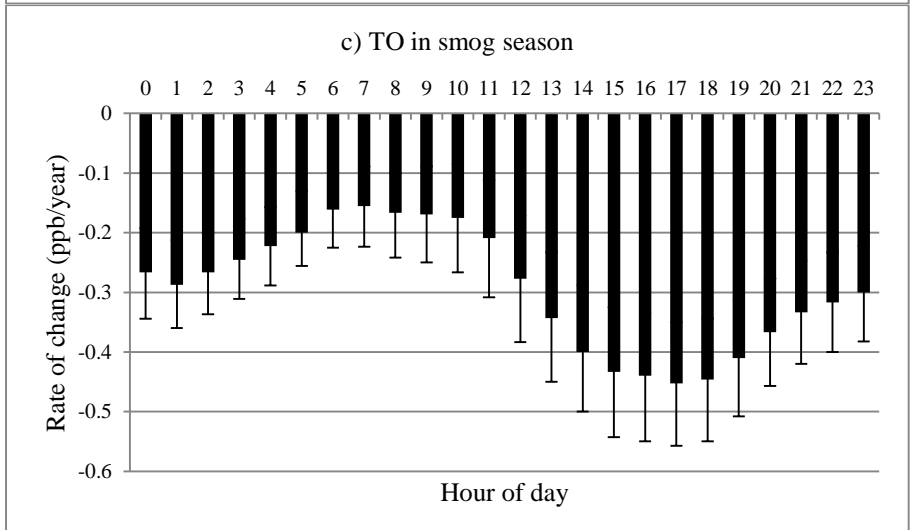
360 During the non-smog season (Figure 9), the rates of change in O₃ and DO₃ were similar as
361 in the case of all months, i.e. the increase in O₃ concentrations could be explained largely by the
362 decreased titration effect. Also similar to that of all months, the rates of change were lower in
363 early morning (5:00-7:00). The greater rates of change were observed in late afternoon and
364 evening (16:00-20:00), instead of at night with all months. The increasing rates of O₃ were
365 higher than the decreasing rates of DO₃ at all hours. The hour-of-day TO trend is overall
366 increasing with less diurnal variation, indicate rising background O₃ levels.



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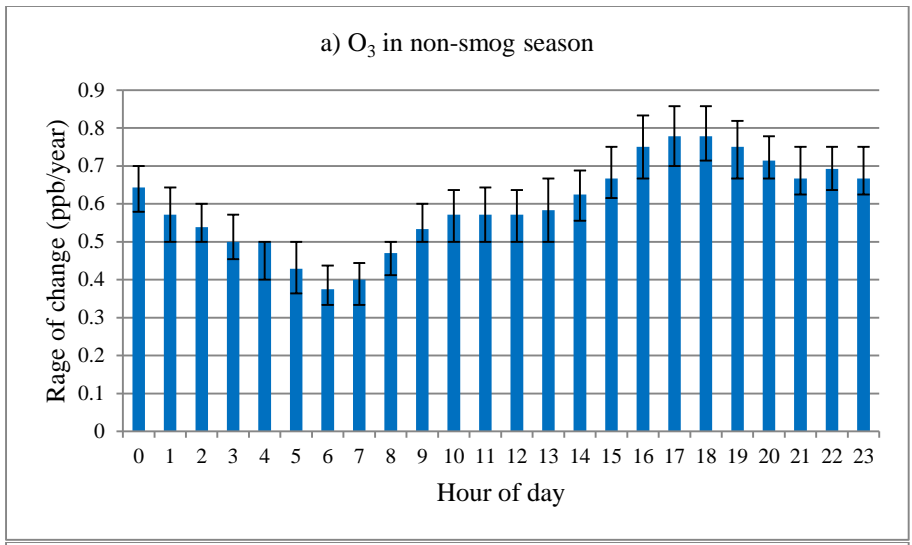


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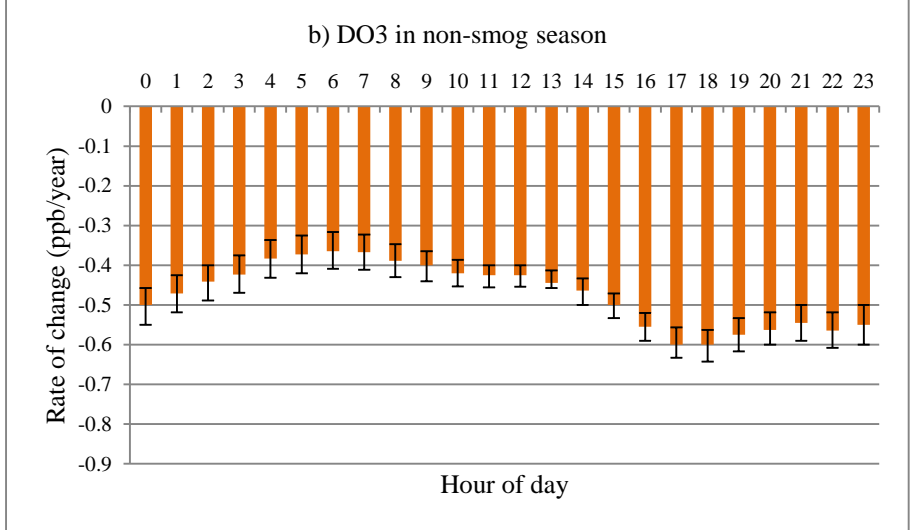
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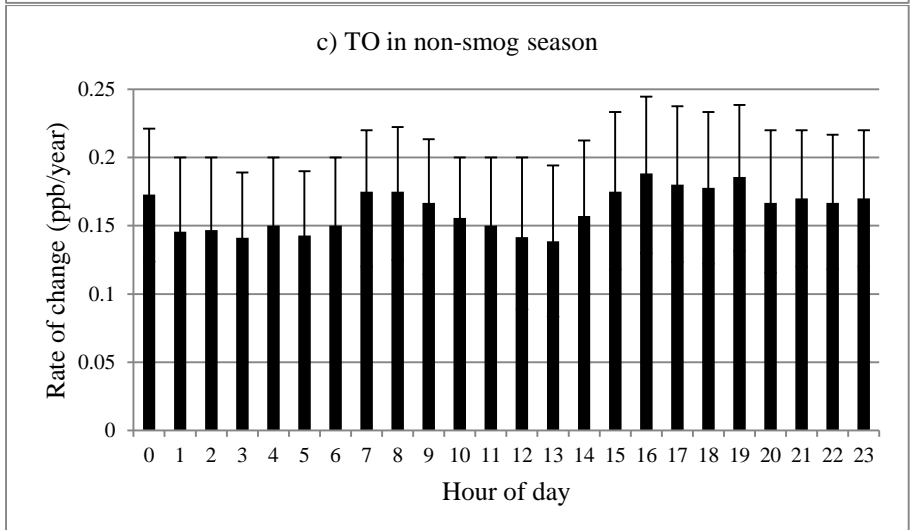
Figure 8. Rate of change by hour-of-day in smog season during 1996-2015 for a) O₃, b) DO₃, and c) TO.



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Figure 9. Rate of change by hour-of-day in non-smog season during 1996-2015 for a) O₃, b) DO₃, and c) TO.

377 **4. Conclusions**

378 This study investigates temporal variations and long-term trends (1996-2015) of ground-
379 level O₃ and its precursors, NO_x and VOCs, in Windsor, Ontario, Canada. The driving force of
380 the observed variations was assessed by studying precursor emissions, photochemical
381 production, NO titration, and background O₃ levels. One of the innovative approaches is the use
382 of TO and trend analysis for different percentiles levels in different seasons and by hour-of-day.

383 O₃ concentrations increased by 33% during 1996-2015 (20.3 ppb in 1996 vs. 27 ppb in
384 2015) in Windsor, while concentrations of NO_x (-58%) and NMHCs (-61%) and OFPs (-73%)
385 decreased significantly during the same time period, owing to effective emission control.
386 Increased O₃ concentrations were observed in all months in a year and all hours in a day, and at
387 all percentile levels with a few exceptions.

388 Our analysis revealed that the increased annual O₃ concentrations in Windsor were caused
389 by the following reasons. First, there were decreased O₃ titration and local photochemical
390 production of O₃, both of which were induced by reduced precursor emissions. The O₃ loss due
391 to the titration decreased by 50% in the 20 years study period, and the declined O₃ titration was
392 observed in all months in a year and all hours in a day. Therefore, the observed increase in O₃
393 concentrations can be largely explained by the decrease in the titration. By removing the titration
394 effect, TO concentrations increased in the non-smog season and decreased in the smog season,
395 resulting in a slightly decreasing trend of annual means during 1996-2015 (-0.076 ppb/year).
396 The declining photochemical production of O₃ is evident by decreased peak O₃ levels (95th
397 percentile) in the smog season as opposed to increased O₃ concentrations at all other percentile
398 levels and all percentiles in the non-smog season. Second, background O₃ level was rising. This
399 is supported by increasing O₃ concentrations in all months in a year and all hours in a day and at
400 all O₃ percentile levels, with the exception of peak O₃ hours and the 95th percentile O₃ levels in
401 the smog season. Furthermore, the increasing rates of O₃ were higher than the decreasing rate of
402 DO₃ at all hours in a day and all percentile levels during the non-smog season when O₃
403 photochemical production is limited.

404 It is apparent that control measures implemented in Ontario and the surrounding regions
405 were effective in curbing NO_x and VOC emissions during the study period of 1996-2015. The

406 reduced O₃ precursors led to decreasing peak O₃ values in the smog season over the past 20
407 years. However, those emission reductions also result in weakened O₃ titration effect in all
408 months in a year and at all hours in a day. Meanwhile, the background O₃ concentrations
409 appeared increasing in the study region, with more impact on the low-to-median levels (i.e. 25th
410 and 50th percentiles) during non-smog season and at night. The net effect of those factors is
411 decreasing peak O₃ levels but an overall increasing annual means in Windsor. The increases in
412 O₃ concentrations in non-smog season (0.58 ppb/year), at night (20:00-8:00, 0.46 ppb/year), and
413 at low-to-median percentiles pose less risk on human health because those O₃ levels are
414 relatively low. The decreasing peak O₃ levels during the smog season is rather beneficial
415 considering the detrimental effects of human exposure to high O₃ concentrations.

416 Our long-term (1996-2015) trends analysis show that annual O₃, NMHC, and OFP levels
417 leveled off after 2008, while NO_x concentrations and the O₃ titration effect appear to
418 continuously decreasing. Considering that O₃ formation in Windsor remains to be VOC-limited,
419 the weakened O₃ titration by NO₂ may lead to slightly increasing O₃ annual means. Moreover,
420 the regional background levels are not expected to decline. Therefore, it is anticipated that O₃
421 concentrations in Windsor may level off or increase slightly in the next few years under similar
422 weather conditions. Due to the complex nature of O₃ formation/consumption and regional
423 transport, it is clear that long-term regional and international efforts are essential to lower O₃
424 concentrations and improve air quality. Results of this study provide insight into the causes of
425 changing O₃ levels in Windsor and how to mitigate O₃ pollution and its adverse effects on
426 human health and the environment. Future studies are warranted to quantify the background O₃
427 level in Windsor area and its long-term trend, and to explore regional transport of O₃ to
428 Windsor.

429

430 **Author contribution**

431 Mr. Tianchu Zhang conducted data analysis and drafted the manuscript. Dr. Xu and Dr. Su
432 designed the study and completed the manuscript.

433

434 **Competing interests**

435 The authors declare that they have no conflict of interest.

436

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441

442 **References**

443 Akimoto, H., Mori, Y., Sasaki, K., Nakanishi, H., Ohizumi, T. and Itano, Y.: Analysis of
444 monitoring data of ground-level ozone in Japan for long-term trend during 1990-2010: Causes
445 of temporal and spatial variation, *Atmos. Environ.*, 102, 302-310, 2015.

446 Aleksic, N., Sedefian, L. and Ku, M.: Empirical estimates of summer background ozone levels
447 in New York State, New York State Department of Environmental Conservation, Albany, NY,
448 2011.

449 Carter, W. P. L.: Development of ozone reactivity scales for volatile organic compounds, *J. Air
450 Waste Manag. Assoc.*, 44(7), 881–899, 1994.

451 Carter, W. P. L.: Documentation of the SAPRC-99 chemical mechanism for VOC reactivity
452 assessment, University of California, Riverside, CA.

453 <http://www.engr.ucr.edu/~carter/pubs/s99doc.pdf> (last access: 4 June 2018), 1999.

454 Chang, K. L., Petropavlovskikh, I., Cooper, O. R., Schultz, M. G. and Wang, T.: Regional trend
455 analysis of surface ozone observations from monitoring networks in eastern North America,
456 Europe and East Asia, *Elem. Sci. Anth.*, 5(50), 2017. Environment and Climate Change Canada
457 (ECCC): Data sources and methods for the air quality indicators.

458 [https://www.ec.gc.ca/indicateurs-indicators/default.asp?lang=En&n=BA9D8D27-
459 1&offset=4&toc=hide](https://www.ec.gc.ca/indicateurs-indicators/default.asp?lang=En&n=BA9D8D27-1&offset=4&toc=hide) (last access: 4 June 2018), 2016.

460 Environment and Climate Change Canada (ECCC): Air pollutant emission inventory – online
461 data search. <http://ec.gc.ca/inrp-npri/donnees-data/ap/index.cfm?lang=En> (last access: 4 June
462 2018), 2018a.

463 Environment and Climate Change Canada (ECCC): NAPS data products. [http://maps-
464 cartes.ec.gc.ca/rnspa-naps/data.aspx](http://maps-cartes.ec.gc.ca/rnspa-naps/data.aspx) (last access: 4 June 2018), 2018b.

465 Fleming, Z. L., Doherty, R. M., von Schneidmesser, E., Malley, C. S., Cooper, O. R., Pinto, J.
466 P., Colette, A., Xu, X., Simpson, D., Schultz, M. G., Lefohn, A. S., Hamad, S., Moolla, R.,

467 Solberg, S. and Feng, Z.: Tropospheric ozone assessment report: Present-day ozone distribution
468 and trends relevant to human health, *Elem. Sci. Anth.*, 6(12), 2018.

469 Gaudel, A. and 58 co-authors: Tropospheric ozone assessment report: Present-day distribution
470 and trends of tropospheric ozone relevant to climate and global atmospheric chemistry model
471 evaluation, *Elem. Sci. Anth.*, 6(39), 2018

472 Gilbert, R. O.: Statistical methods for environmental pollution monitoring, Van Nostrand
473 Reinhold Company Inc, New York, NY, 1987.

474 Huryn, S. and Gough, W.: Impact of urbanization on the ozone weekday/weekend effect in
475 Southern Ontario, Canada, *Urban Clim.*, 8, 11-20, 2014.

476 International Global Atmospheric Chemistry (IGAC), Tropospheric Ozone Assessment Report.
477 <http://www.igacproject.org/activities/TOAR> (last access: 16 October 2018), 2018.

478 Iowa Department of Natural Resources (IDNR): Effects of ground-level ozone.
479 <http://www.iowadnr.gov/Environmental-Protection/Air-Quality/Air-Pollutants/Effects-Ozone>
480 (last access: 4 June 2018), 2018.

481 Itano, Y., Bandow, H., Takenaka, N., Saitoh, Y., Asayama, A. and Fukuyama, J.: Impact of
482 NO_x reduction on long-term ozone trends in an urban atmosphere, *Sci. Total Environ.*, 379(1),
483 46-55, 2007.

484 Itano, Y., Yamagami, M. and Ohara, T.: Estimation of primary NO₂/NO_x emission ratio from
485 road vehicles using ambient monitoring data, *Studies Atmos. Sci.*, 1, 1-7, 2014.

486 Jaffe, D., Price, H., Parrish, D., Goldstein, A. and Harris, J.: Increasing background ozone
487 during spring on the west coast of North America, *Geophys. Res. Lett.*, 30(12), 1-4, 2003.

488 Jia, C., Mao, X., Huang, T., Liang, X., Wang, Y., Shen, Y., Jiang, W., Wang, H., Bai, Z., Ma, M.
489 and Yu, Z.: Non-methane hydrocarbons (NMHCs) and their contribution to ozone formation
490 potential in a petrochemical industrialized city, Northwest China, *Atmos. Res.*, 169, 225-236,
491 2016.

492 Jun, T., Xia, Z. G., Wang, H. and Li, W.: Temporal variations in surface ozone and its
493 precursors and meteorological effects at an urban site in China, *Atmos. Res.*, 85(3-4), 310-337,
494 2007.

495 Koo, B., Jung, J., Pollack, A. K., Lindhjem, C., Jimenez, M. and Yarwood, G.: Impact of
496 meteorology and anthropogenic emissions on the local and regional ozone weekend effect in
497 Midwestern US, *Atmos. Environ.*, 57, 13-21, 2012.

498 Kurtenbach, R., Kleffmann, J., Niedojadlo, A. and Wiesen, P.: Primary NO₂ emissions and their
499 impact on air quality in traffic environments in Germany, *Environ. Sci. Europe.*, 24(21), 1-8,
500 2012.

501 Lin, C. Y. C., Jacob, D. J., Munger, J. M. and Fiore, A. M.: Increasing background ozone in
502 surface air over the United States, *Geophys. Res. Lett.*, 27(21), 3465-3468, 2000.

503 Mills, G., Pleijel, H., Malley, C. S., Sinha, B., Cooper, O. R., Schultz, M. G., Neufeld, H. S.,
504 Simpson, D., Sharps, K., Feng, Z., Gerosa, G., Harmens, H., Kobayashi, K., Saxena, P.,
505 Paoletti, E., Sinha, V. and Xu, X.: Tropospheric ozone assessment report: Present-day
506 tropospheric ozone distribution and trends relevant to vegetation, *Elem. Sci. Anth.*, 6(47), 2018.

507 Ministry of the Environment (MOE): Air Quality in Ontario 2006 Report, Queen's Printer for
508 Ontario, PIBS 6041e, 2006.

509 Ministry of the Environment (MOE): Air Quality in Ontario Report for 2010, Queen's Printer
510 for Ontario, PIBS 8640e, 2012.

511 Ministry of the Environment and Climate Change (MOECC): Air Quality in Ontario 2015
512 Report, Queen's Printer for Ontario, ISSN 1710-8136, 2017.

513 Ministry of the Environment, Conservation and Parks (MECP): Search: air pollutant data,
514 <http://airqualityontario.com/history/index.php> (last access: 4 June 2018), 2018.

515 National Academy of Sciences (NAS): Ozone-forming potential of reformulated gasoline. The
516 National Academies Press, Washington, DC. <https://www.nap.edu/read/9461/chapter/5> (last
517 access: 4 June 2018), 1999.

518 Parrington, M., Palmer, P. I., Lewis, A. C., Lee, J. D., Rickard, A. R., Di Carlo, P., Taylor, J. W.,
519 Hopkins, J. R., Punjabi, S., Oram, D. E., Forster, G., Aruffo, E., Moller, S. J., Bauguitte, S. J.,
520 Allan, J. D., Coe, H. and Leigh, R. J.: Ozone photochemistry in boreal biomass burning plumes,
521 *Atmos. Chem. Phys.*, 13, 7321-7341, 2013.

522 Pudasainee, D., Sapkota, B., Shrestha, M. L., Kaga, A., Kondo, A. and Inoue, Y.: Ground level
523 ozone concentrations and its association with NO_x and meteorological parameters in Kathmandu
524 Valley, Nepal, *Atmos. Environ.*, 40(40), 8081-8087, 2006.

525 Schultz, M. G. and 96 co-authors: Tropospheric ozone assessment report: Database and metrics
526 data of global surface ozone observations, *Elem. Sci. Anth.*, 5(58), 2017.

527 Sen, P. K.: Estimates of the regression coefficient based on Kendalls Tau, *J. Am. Stat. Assoc.*,
528 63(324), 1379-1389, 1968.

529 Shin, H. J., Cho, K. M., Han, J. S., Kim, J. S. and Kim, Y. P.: The effects of precursor emission
530 and background concentration changes on the surface ozone concentration over Korea, *Aerosol*
531 *Air Qual. Res.*, 12(1), 93-103, 2012.

532 Sicard, P., Dalstein-Richier, L. and Vas, N.: Annual and seasonal trends of ambient ozone
533 concentration and its impact on forest vegetation in Mercantour National Park (South-eastern
534 France) over the 2000-2008 period, *Environ. Pollut.*, 159(2), 351-362, 2011.

535 Sillman, S.: The relation between ozone, NO_x and hydrocarbons in urban and polluted rural
536 environments, *Atmos. Environ.*, 33(12), 1821-1845, 1999.

537 Simon, H., Reff, A., Wells, B. Xing, J. and Frank, N.: Ozone trends across the United States
538 over a period of decreasing NO_x and VOC Emissions, *Environ. Sci. Technol.*, 49, 186-195,
539 2015.

540 So, K. L. and Wang, T.: On the local and regional influence on ground-level ozone
541 concentrations in Hong Kong, *Environ. Pollut.*, 123(2), 307-317, 2003.

542 United States Environmental Protection Agency (USEPA): The relationships between NO_x,
543 NO_y, and ozone. <https://www3.epa.gov/ttnamti1/files/ambient/pams/97workbook10.pdf> (last
544 access: 16 August 2018), 2000.

545 United States Environmental Protection Agency (USEPA): Implementation of the 2015 primary
546 ozone NAAQS: Issues associated with background ozone.
547 <https://www.epa.gov/sites/production/files/2016-03/documents/whitepaper-bgo3-final.pdf> (last
548 access: 4 June 2018), 2015.

549 United States Environmental Protection Agency (USEPA): Health effects of ozone pollution.
550 <https://www.epa.gov/ozone-pollution/health-effects-ozone-pollution> (last access: 4 June 2018),
551 2018.

552 Wang, Y., Wang, H., Guo, H., Lyu, X., Cheng, H., Ling, Z., Louie, P. K. K., Simpson, I. J.,
553 Meinardi, S. and Blake, D. R.: Long term O₃-precursor relationships in Hong Kong: Field
554 observation and model simulation. *Atmos. Chem. Phys.*, 17, 10919-10935, 2017.

555 Yan, Y., Peng, L., Li, R., Li, Y., Li, L. and Bai, H.: Concentration, ozone formation potential and
556 source analysis of volatile organic compounds (VOCs) in a thermal power station centralized
557 area: A study in Shuozhou, China, *Environ. Pollut.*, 223, 295-304, 2017.

558 Zhang, T.: Long-term trend of ground-level ozone through statistical and regional transport
559 analysis, Master thesis, University of Windsor, Windsor, Ontario, Canada.
560 <http://scholar.uwindsor.ca/etd/5880/> (last access: 4 June 2018), 2016.